

# PATENT SPECIFICATION

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 (72) Inventors CARLO NICORA, ANDREA MATTIUSSI and  
 ANTONIO VANDI



## (54) THERMOPLASTIC MOULDING COMPOSITIONS

- (71) We, MONTECATINI EDISON S.p.A., an Italian Company of 31 Foro Buonaparte, Milan, Italy, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- This invention relates to thermoplastic moulding compositions suitable for injection moulding, based on saturated linear polyesters of the kind derived from one or more aromatic dicarboxylic acids, with or without a minor amount of aliphatic dicarboxylic acid, and saturated aliphatic or cycloaliphatic glycols, and optionally in which the alcohol component thereof includes up to 1% by weight of tetrols, and polyesters derived from hydroxy carboxylic acids.
- It is known that thermoplastic resins based on saturated polyesters of dicarboxylic acids may be utilized for preparing manufactured articles by injection moulding or extrusion. Polyethylene terephthalate, in particular, exhibits excellent physical properties when it is in the crystalline form, and it may be used for mechanical applications requiring high performances. Nevertheless, the molten polyethyleneterephthalate crystallizes rather slowly, the moulded articles present internal stresses due partially to a non-uniform growth of the spherulites and to long crystallization times.
- The addition of nucleating agents increases the crystallization rate, thus providing a large number of centres which initiate the formation of the spherulites. It has been already proposed to use, as nucleating agents, solid finely subdivided inorganic matter, with a view to increasing the crystallization rate of the polyester mass injected into the mould. In this way it is possible to attain an increase in the crystallinity and density of the finished parts, and, by consequence, an improvement in both the dimensional stability and shape stability at high temperatures. Metal oxides, salts of alkaline-earth metals, talc, glass powder or metals have been cited as examples of suitable inorganic solid matters, usually with a particle size below 5  $\mu$ .
- In general, these inorganic powders can be dispersed homogeneously only with difficulty in the polyester mass, and it often happens that the moulded parts stick to the mould walls, causing considerable complications during the moulding operation. Agglomerates of the powder particles lead to a lowering of the impact strength of the finished article.
- The inorganic nucleating agents may be used in combination with some liquid materials capable of encouraging further the polyethylene terephthalate crystallization. Such agents may moreover be employed together with materials such as aromatic sulphonates to facilitate mould release. However, the aromatic sulphonates cannot entirely replace the inorganic nucleants, as they do not possess nucleating properties. It is therefore desirable to have available a nucleating agent which is easily and uniformly dispersible in the polyester mass, thus allowing the polymer crystallization time to be reduced and to obtain, by means of relatively short moulding cycles, well formed parts of good dimensional stability.
- It has now been found that it is possible to prepare thermoplastic moulding compositions having a high crystallization rate and allowing relatively short moulding cycles by compounding a linear saturated polyester of the kind referred to with from 0.05 to 1.5% by weight, preferably from 0.1 to 1.0% by weight, with respect to the polyester of at least one organic sulphonate salt, in which the organic sulphonate salt is an alkali metal or alkaline-earth metal isethionate or a derivative thereof, an alkali metal or alkaline-earth metal salt of taurine or a derivative thereof, or an ester of an alkali metal or alkaline-earth metal sulphonylsuccinate.

The organic sulphonate salts used in the moulding compositions of this invention act both as nucleants and as mould release agents. Since they melt during processing, a finer subdivision in the polyester is obtained, and hence a higher efficiency in comparison with that attainable, for instance, by merely adding inorganic solid matters. Furthermore, these salts do not give rise to agglomerates in the polyester, which, conversely, are found when solid inorganic matters only are added.

Addition of the sulphonate salts makes it possible to shorten remarkably the injection cycle, and, by consequence, increase the production rate, without prejudicing the technical characteristics of the polyester as regards its application.

It is possible not only partially to substitute the inorganic solid powders by the above sulphonate salts: such powders may be entirely omitted, provided that sufficient amounts of sulphonate salts are incorporated.

Sodium isethionate and its derivatives, for example sodium acetyl-isethionate and the ester of sodium acetyl-isethionate with long chain fatty acids such as the acids derived from coconut; the alkali metal and alkaline-earth metal salts of taurine and their derivatives, such as sodium N-methyl-N-palmitoyl taurate; and esters of sodium sulphosuccinate, such as sodium diisooctyl-sulphosuccinate may be suitably utilized as organic sulphonate salts.

The sulphonate salts used may be added to the polyester either when preparing the same, before or during the polycondensation, or to the already prepared polymer. In this latter case the dispersion of the sulphonic salt on granules of the polyester may be effected by means of a solvent or directly in a rotary drum. To attain a better homogenisation the so-coated granules should be preferably regranulated in an extruder. Polyethylene terephthalate is particularly suitable as the polyester. It is however possible also to use other polyesters, for instance polycyclohexane-1,4-dimethylol terephthalate. Further suitable polyesters are those containing, as acid component, in addition to terephthalic acid, minor amounts, generally up to 5 mole%, of other dicarboxylic aromatic or aliphatic acids, e.g. isophthalic, naphthalene-2,6-dicarboxylic, or adipic acid. As the alcohol component, besides ethylene-glycol there may be used for example up to 30% by moles of other aliphatic diols, such as 2,2-dimethylpropanediol-1,3 or 1,4-butanediol, or up to 1% by weight of tetrols, for instance, 1,1,4,4-tetramethylolcyclohexane. Polyesters derived from hydroxycarboxylic acids may also be employed.

The polyesters desirably have an intrinsic viscosity (measured in a phenol:tetrachloroethane solution of 50:50 weight ratio, at 25°C) ranging from 0.5 to 2.0 dl/g, preferably from 0.8 to 1.6 dl/g. When the desired intrinsic viscosity values cannot be reached by

poly-condensation in the molten state, resort may be had to polymerization in the solid state effected with granules of suitable size either before or after addition of the organic sulphonate.

The polyester granules may be coated with 0.01 to 1% by weight, preferably with 0.05 to 0.5% by weight still more preferably 0.1 to 0.4% by weight with respect to the polyester, of waxes having a melting point of 50° to 150°C.

The intrinsic viscosity of the manufactured product desirably ranges from 0.5 to 1.6 dl/g, preferably from 0.7 to 1.3 dl/g. Such values may be obtained either by molding a polymer having a slightly higher intrinsic viscosity, or by raising the polymer intrinsic viscosity during moulding or during a preliminary extrusion by addition of polyfunctional materials capable of reacting with the polymer terminal groups.

To the moulding resin formulation other additives may be added, such as: inorganic nucleating agents (e.g. talcum, pyrophyllite, and calcium carbonate), pigments and also organic modifiers, with a view to improving the impact strength (for instance a cross-linked rubber).

To obtain crystalline manufactured products having optimum dimensional stability, the mould should be regulated at a temperature of from 100° to 150°C.

The effect of the sulphonate salts on the crystallization rate of the polyester has been determined by measuring, by means of a differential calorimeter, the temperature at which the crystallization reaches its peak ( $T_c$ ). Such measurements have been carried out by cooling, at two different cooling rates (16° and 32°C/min.) samples brought to 30–40°C above their melting point, in order to eliminate any trace of "crystalline memory". The higher the  $T_c$ , the more intense the nucleating effect exerted by the sulphonate salt. The calorimeter utilized for the purpose was of the PERKIN-ELMER DSC/16 type.

Polyester granules prepared according to the various different methods hereinbefore referred to have been employed also for the production, by injection moulding, of test discs (diameter 10 cm; thickness 3 mm), the moulding cylinder and the mould temperatures being about 285°C and 140°C respectively. The processing cycle has been varied by selecting times of residence in the mould ranging from 7 to 100 seconds. Thus it has been possible to ascertain which is the minimum residence time required to obtain an article which does not deform during ejection or whilst cooling down to room temperature. Times over 100 sec. have not been considered, as they are of no interest from a practical viewpoint. This residence time is a function of two different parameters, namely: the polymer crystallization rate and the capability of the manufactured product to leave the mould. The residence times in the mould

will be the shorter, the more effective is the sulphonate salt additive as nucleant and as lubricant.

- 5 The following examples and comparative examples are given to illustrate how the invention may be carried into effect.

#### EXAMPLE 1.

- 10 500 g of an ester obtained by reacting terephthalic acid with ethylene glycol and having a glycol/acid total molar ratio of approx. 1.3:1 are blended with 0.033 g of  $Sb_2O_3$  and melted in a polycondensation reactor. 0.133 g of  $H_3PO_3$  is incorporated at a temperature of 230°C; subsequently, in 1 hour the tempera-

ture is gradually brought to 285°C, while the pressure is reduced to 0.1—0.3 mm Hg. The reaction is maintained until a polymer has formed having an intrinsic viscosity of 0.6—1.0 dl/g. An organic sulphonate salt is added either together with  $H_3PO_3$  (method A) or 30 minutes after having reached 285°C (method B). Table 1 indicates the results obtained from differential calorimetric tests on samples containing various different sulphonate salts. These results show that, taking into account the concentrations, the sulphonate salts most efficient as nucleating agents are those used in accordance with the present invention.

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TABLE I

Nucleant	Method of addition	Nucleant weight/100 g of polymer	Millimol of nucleant/100 g of polymer	Intrinsic viscosity dl/g	T <sub>C</sub> °C at a cooling rate	
					16°C/min	32°C/min
—	—	—	—	0.73	174	155
Fenopon AC 78 (1)	B	0.5	1.47	0.66	209	193
Fenopon AC 78	A	0.25	0.73	0.65	179	166
Fenopon TN 74 (2)	B	0.5	1.25	0.67	200	178
Na-diisooctylsulphosuccinate	A	0.5	1.12	0.66	199	190
„	B	0.5	1.12	0.68	207	193
„	A	1.0	2.25	0.66	194	187
Na-acetyl-isethionate	B	0.5	2.63	0.60	210	199
„	B	0.75	3.94	0.64	206	193
Na-isethionate	B	0.5	3.4	0.89	202	192
Na-p-toluene sulphonate (Comparative)	A	0.5	2.58	0.62	185	172
Na-dodecylbenzenesulphonate (88% pur.) (Comparative)	A	0.5	1.26	0.95	163	—
Na-dimethylsulphoisophthalate (Comparative)	A	0.5	1.69	0.72	182	166

## Footnotes to Table 1

- (1) Trade name of the ester of Na-isethionate with coconut acids (General Aniline and Film Corporation).
- (2) Trade name of sodium N-methyl-N-palmitoyltaurate (General Aniline and Film Corporation).

## EXAMPLE 2.

7.5 g of an ester material prepared by continuous esterification of terephthalic acid with ethylene glycol and having a glycol/acid total molar ratio of 1.26:1 are melted in a polycondensation reactor, whilst gradually raising the temperature. At 230°C, 2.02 g of H<sub>3</sub>PO<sub>3</sub> are added and at 250°C 1.40 g of Sb<sub>2</sub>O<sub>3</sub>. As from 250°C the pressure is gradually reduced, while the temperature is increased until values of 277°C and of 0.1 mm Hg of residual pressure are reached. About 1 hour after attainment of aforesaid conditions, a sulphonate salt is added in an amount of 0.5% by weight calculated on the final polymer. Polyconden-

sation is carried on for further 25—30 minutes until the desired intrinsic viscosity is reached. The polymers is then extruded in the form of strands and cut to chips by means of a slitting machine. After drying, the polymer is subjected to a treatment in a rotary drum in order to increase its intrinsic viscosity. The conditions are as follows: 220°C, 0.02 mm Hg, 30—60 hours depending on the initial and final viscosity.

In an analogous comparative test no sulphonate salt is added. Table 2 indicates for each polymer sample, the data determined by a differential calorimetric test as well as the minimum residence time in the mould.

TABLE 2

Sample	Nucleant	Viscosity (dl/g) [ $\eta$ ]	Tc (°C) at a cooling rate of		Min. residence time in the mold in seconds
			16° min.	32°/min.	
A	—	1.15	172.4	157.6	> 100
B	Na-acetyliseithionate	1.1	208.6	194.9	90
C	sodium diisooctylsulphosuccinate	1.05	205.0	191.4	90
D	Fenopen TN 74	1.22	187.2	171.3	90
E	Fenopon AC 78	1.20	204.2	197.2	45

## EXAMPLE 3.

100 parts by weight of polyethylene terephthalate granules having a moisture content lower than 0.02% by weight and an intrinsic viscosity of 1.40 dl/g (determined in a 50:50 phenol/tetrachloroethane solution at 25°C) are rolled for 1 hour with 0.5 parts by weight of a suphonate salt. The granules so coated are homogenized at a temperature of about 275°C in an extruder. The granulate is then dried again to a moisture content lower than 0.02% by weight. Its intrinsic viscosity is from 1.10 to 1.20 dl/g. This granulate is then used to

obtain, by injection moulding, discs having diameters of 10 cm and thicknesses of 3 mm, the temperature of the moulding cylinder being approximately 285°C and that of the mould 140°C. The results are set out in Table 3.

Also sample F, free from any nucleant, obtained by subjecting the starting polyethylene terephthalate to the same treatment (extrusion, drying, etc.) is included as a control. The discs obtained from the polymers treated with a nucleating agent have a density of 1.385 g/cm<sup>3</sup>, while the disc obtained from sample F has a density of 1.375 g/cm<sup>3</sup>.

TABLE 3

Sample	Nucleant	T <sub>c</sub> (°C) at a cooling rate of		Minimum residence time in the mold in seconds
		16°C/min.	32°C/min.	
F	—	194.8	179.7	100
G	sodium acetyl-sulfonate	218.1	203	35
H	sodium diisooctyl-sulphosuccinate	208.6	191.8	90
I	Fenopon TN 74	199.8	183.9	25
L	Fenopon AC 78	201.3	190.2	25

## EXAMPLE 4.

According to the method described in Example 3, two samples (M and N of Table 4) of polyethylene terephthalate are prepared, having an intrinsic viscosity of 0.55 dl/g, the former containing 0.5 parts by weight of Fenopon AC 78 and the latter containing 0.5 parts by weight of Fenopon AC 78 as well as 0.45 parts by weight of talcum, based on

100 parts by weight of polymer. The intrinsic viscosity of the granulate is then brought, by post-polymerization in the solid phase (at 225°C for 40 hours at a pressure of 0.1 mm Hg), to 1.18 dl/g. The samples are then subjected to the tests indicated in preceding Examples. The resulting data are set out in Table 4.

TABLE 4

Sample	Nucleant	T <sub>c</sub> (°C) at a cooling rate of		Minimum residence time in the mold in seconds
		16°C/min.	32°C/min.	
M	Fenopon AC 78	205	194.4	20
N	Fenopon AC 78 + talcum	208.2	197	40

## EXAMPLE 5.

Granules of polyethylene terephthalate (100 parts by weight), having a moisture content lower than 0.02% by weight and an intrinsic viscosity of 1.40 dl/g (measured in a 50:50 phenol/tetrachloroethane solution at 25°C), are rolled for 1 hour with 0.5 parts by weight of Fenopon AC 78 and 20 parts by weight of a cross-linked elastomer of the methylmethacrylate-butadiene-styrene type (trade name: Kureha BTA III). The mixture thus obtained is re-granulated in an extruder at 275°C. Subsequently, the granulate is dried to a moisture content lower than 0.02% by weight. Its intrinsic viscosity is 1.19 dl/g.

T<sub>0</sub> of 205° and 194.5°C for cooling rates of 16°C/min and 32°C/min respectively are found for the product. The minimum residence time in the mould is 25 seconds and the manufactured product density is 1.390 g/cm<sup>3</sup>. The

Izod impact strength on notched test specimens obtained from a disc of the product has given values ranging from 13 to 15 kg cm/cm as against values of 2 to 3 kg cm/cm determined on a comparative control product free from any impact strength improving agent.

## WHAT WE CLAIM IS:—

1. A thermoplastic moulding composition comprising a linear saturated polyester of the kind referred to and from 0.05 to 1.5% by weight with respect to the polyester of at least one organic sulphonate salt, in which the organic sulphonate salt is an alkali metal or alkaline-earth metal isethionate or a derivative thereof, an alkali metal or alkaline-earth metal salt of taurine or a derivative thereof, or an ester of an alkali metal or alkaline-earth metal sulpho-succinate.

2. A composition as claimed in Claim 1 in

which the said organic sulphonate salt is present in an amount of from 0.1 to 1.0% by weight.

5 3. A composition as claimed in Claim 1 or 2 in which the said organic sulphonate salt is sodium isethionate or a derivative thereof.

4. A composition as claimed in Claim 1 or 2 in which the said organic sulphonate salt is an ester of sodium sulposuccinate.

10 5. A composition as claimed in any of Claims 1 to 4 also containing an inorganic solid nucleant.

15 6. A composition as claimed in any of Claims 1 to 5 in which the polyester has an intrinsic viscosity (measured in a phenol:tetrachloroethane solution of 50:50 weight ratio, at 25°C) of from 0.5 to 2.0 dl/g.

20 7. A composition as claimed in any of Claims 1 to 6 in which the polyester used is polyethylene terephthalate.

8. A composition as claimed in any of Claims 1 to 7 in the form of granules coated

with from 0.01 to 1% by weight of a wax having a melting point of 50° to 150°C.

9. A composition as claimed in Claim 8 in which the granules are coated with from 0.05 to 0.5% by weight of the said wax. 25

10. A composition according to Claim 1 substantially as described in any of the foregoing Examples. 30

11. A formed article obtained from a composition according to any of the foregoing claims and having an intrinsic viscosity (measured in a phenol:tetrachloroethane solution of 50:50 weight ratio, at 25°C) of from 0.5 to 1.6 dl/g. 35

12. A formed article as claimed in Claim 11 having an intrinsic viscosity of from 0.7 to 1.3 dl/g.

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